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Published in:
Physical Review B Condensed Matter

Link to article, DOI:
[10.1103/PhysRevB.69.041403](https://doi.org/10.1103/PhysRevB.69.041403)

Publication date:
2004

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Morikawa, Y., Ishii, H., & Seki, K. (2004). Theoretical study of n-alkane adsorption on metal surfaces. *Physical Review B Condensed Matter*, 69(4), 041403. <https://doi.org/10.1103/PhysRevB.69.041403>

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Theoretical study of *n*-alkane adsorption on metal surfacesYoshitada Morikawa,^{1,2,*} Hisao Ishii,³ and Kazuhiko Seki⁴¹Research Institute for Computational Sciences (RICS), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan²Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark³Research Institute of Electrical Communication, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan⁴Research Center for Materials Science, Institute for Advanced Research, and Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

(Received 14 July 2003; published 23 January 2004)

The interaction between *n*-alkane and metal surfaces has been studied by means of density-functional theoretical calculations within a generalized gradient approximation (GGA). We demonstrate that although the GGA cannot reproduce the physisorption energy well, our calculations can reproduce the experimentally observed work-function change and softening of the CH stretching mode reasonably well. We also show that the most significant factor determining their dependence on metal substrates is the distance between the molecule and the substrate.

DOI: 10.1103/PhysRevB.69.041403

PACS number(s): 73.20.-r, 73.30.+y, 73.61.-r, 85.65.+h

The formation of an interfacial dipole layer during organic molecular adsorption on metal surfaces has been attracting enormous attention, since it is directly related to the carrier injection barrier between organic molecules and metal electrodes in organic devices.¹⁻⁴ Interfacial dipole layers between various kinds of molecules including *n*-alkanes and several metal surfaces were measured and summarized.^{1,2} Ishii and Seki pointed out two major trends (i) in most cases, organic molecules reduce the metal work function and (ii) the magnitude of the interfacial dipole tends to increase as the substrate metal work function increases. It is desired to elucidate the origin of these trends, with the clarification of important factors determining the substrate dependence.

Because the adsorption energies E_{ad} of *n*-alkane molecules on metal surfaces are rather small (of the order of 10 kJ/mol/CH₂ chain⁵) the molecule-surface interaction has been considered to be quite weak and categorized to be a typical physisorption state. However, formation of a large interfacial dipole¹ and significant softening of the CH stretching [$\nu(\text{CH})$] mode⁶ were reported for *n*-alkane and cyclic alkane adsorbed on metal surfaces. Ishii and Seki suggested two origins for the interfacial dipole formation by physisorbed molecules, i.e., the image effect and the push back effect.¹ Very recently, Bagus *et al.* demonstrated the importance of exchangelike effects for the interfacial dipole formation.³ The origin of the $\nu(\text{CH})$ mode softening was ascribed to a kind of hydrogen bonding between the CH group and the substrate, and a correlation between the magnitude of the $\nu(\text{CH})$ softening and the reactivity of the substrate metal towards the dehydrogenation of alkanes was pointed out,^{6,7} but such a simple correlation is not observed for some systems.⁸ Recently, Yamamoto *et al.*⁹ proposed the transition dipole-image dipole interaction and Fossler *et al.* and Öström *et al.*^{10,11} argued the charge transfer from metal states to molecular unoccupied states to be the origin of the $\nu(\text{CH})$ mode softening.

In this paper, we report a study of interfacial dipole layer formation and vibrational mode softening of *n*-alkane ad-

sorbed on various metal surfaces using density-functional theory^{12,13} (DFT) calculations within a generalized gradient approximation (GGA).¹⁴ All our calculations were carried out using program package STATE (simulation tool for atom technology) which has been successfully applied for semiconductor as well as metal surfaces.¹⁵ The electron-ion interaction was described by pseudopotentials^{16,17} and wave functions and the charge density were expanded by a plane-wave basis set with the cutoff energies of 36 Ry and 400 Ry, respectively. Substrate surfaces were described by six-layer slabs, which are infinitely repeated periodically in all three directions and vacuum regions of ~ 2.0 nm are inserted between slabs. 12×12 uniform mesh points were used for **k**-point sampling in the surface Brillouin zone for 1×1 surface unit cell and similar mesh points were used for other surface unit cells. Using these techniques, calculated bulk equilibrium lattice constants and surface work functions agree well with experimental results as summarized in Table I.

To see the ability and the limitation of DFT-GGA calculations for describing *n*-alkanes adsorbed on metal surfaces, we first investigated the adsorption state of polyethylene (CH₂)_{*n*}, which is the long-chain limit of *n*-alkanes, on the Cu(100) surface and compared calculated results with experimental ones. Experimentally, it was concluded that the *n*-alkane molecule is lying down with its molecular C-C-C plane parallel to the surface, with its molecular axis parallel to the [110] direction, and with two times periodicity along the direction perpendicular to the molecular axis.²⁰⁻²⁵ Because the second nearest-neighbor C-C distance of 0.2534 nm is close to the nearest-neighbor Cu distance of 0.2576 nm, we used a 1×2 unit cell to simulate the polyethylene adsorbed Cu(100) surface as shown in Fig. 1(a). We fixed the C height (normal to the surface, denoted by Z_C , hereafter) at different values and all other molecular degrees of freedom are relaxed. Z_C is measured from the plane of the nuclei of the first-layer atoms. We also checked the stability of the deduced structure with respect to molecular positions parallel

TABLE I. Calculated and experimental values of bulk lattice constants and surface work functions of metals.

		Lattice constants				Work function		
		Calculated		Expt. ^a		Calculated		Expt. ^b
Metal		<i>a</i> /nm	<i>c</i> / <i>a</i>	<i>a</i> /nm	<i>c</i> / <i>a</i>	Surface	ϕ /eV	ϕ /eV
Mg	hcp	0.321	1.601	0.321	1.624	(001)	3.72	3.66 ^c
Al	fcc	0.405		0.405		(111)	4.09	4.24
Cu	fcc	0.364		0.361		(100)	4.51	4.59
Ru	hcp	0.272	1.578	0.270	1.584	(001)	5.03	4.71 ^c
Ag	fcc	0.408		0.409		(111)	4.46	4.74
Pt	fcc	0.392		0.392		(111)	5.76	5.70
Au	fcc	0.415		0.408		(111)	5.15 ^d	5.31

^aReference 18.^bReference 19.^cPolycrystal.^dThe ($\sqrt{3} \times 23$) reconstruction is not taken into account.

to the surface. Polyethylene adsorbed between two Cu atomic rows is slightly more stable than that adsorbed on a Cu atomic row, but the energy difference is small (~ 0.2 kJ/mol/CH₂). Therefore, we used the molecular adsorption geometry shown in Fig. 1(a). The vibrational normal-mode analysis was then carried out. The Z_C degree of freedom was also included in the normal-mode analysis. E_{ad} the work-function change $\Delta\phi$, which is proportional to the negative value of the induced interfacial dipole moment per unit surface area, and the $\nu(\text{CH})$ frequencies of polyethylene adsorbed on Cu(100) are summarized in Table II along with the $\nu(\text{CH})$ frequencies of crystalline polyethylene. For polyethylene/Cu(100), only vibrational modes at the Γ point of the surface Brillouin zone were calculated. Since there are four C-H bonds in a unit cell, there are four $\nu(\text{CH})$ modes at the Γ point. In the case of crystalline polyethylene, we used the experimentally observed unit cell [orthorhombic, $a = 0.74$ nm, $b = 0.493$ nm, $c = 0.2534$ nm (Refs. 26 and 27)] which contains two mutually nearly orthogonal alkyl chains in a unit cell. Because of the vibrational mode coupling between the two chains in a unit cell, each $\nu(\text{CH})$ mode splits into two modes and eight $\nu(\text{CH})$ modes appear. Still the splitting by the intermolecular interaction is small (less than

4 cm⁻¹), and we took the averaged values.

As seen in Table II, the total energy takes minimum at $Z_C = 0.38$ – 0.39 nm, but E_{ad} is much smaller than the experimental value of ~ 6 kJ/mol/CH₂ (Ref. 28) due to the well-known deficit of GGA. However, we show below that the work-function change and the softening of the CH stretching mode can be well reproduced by the present calculations. Table II shows that two of the four $\nu(\text{CH})$ modes soften dramatically as the molecule approaches to the surface. As suggested before,⁹ the lower two $\nu(\text{CH})$ modes are mainly ascribed to the stretching modes between C and H_{*p*} (the proximate H to the surface), while the upper two $\nu(\text{CH})$ modes are mainly ascribed to the stretching modes between C and H_{*f*} (the H farther away from the surface). To determine the equilibrium distance between the surface and C atoms more reliably, we compared the calculated $\nu(\text{CH})$ modes with experimentally observed ones.²⁴ Hosoi *et al.* reported a frequency of ~ 2800 cm⁻¹ for the softened $\nu(\text{CH}_p)$ mode, which is 48 cm⁻¹ lower than the $\nu_s(\text{CH})$ frequency of the crystalline polyethylene. Because the calculated $\nu(\text{CH})$ frequencies are higher than the experimental values, we calculated frequency shifts from the crystalline polyethylene and compared them with experimental values. We define $\Delta\nu(\text{CH}_p)$ as the frequency difference between the lowest $\nu(\text{CH}_p)$ mode and the dipole-active $\nu_s(\text{CH})$ mode of crystalline polyethylene [the second lowest $\nu(\text{CH})$ mode]. At $Z_C = 0.378$ nm, $\Delta\nu(\text{CH}_p)$ and $\Delta\phi$ become -48 cm⁻¹ and -0.36 eV, respectively, which are close to the experimental values of -48 cm⁻¹ and -0.3 eV,²² respectively. Therefore, our calculations consistently reproduce both $\Delta\nu(\text{CH}_p)$ and $\Delta\phi$, and strongly suggest that the equilibrium distance between C atoms of *n*-alkane and the first-layer Cu atoms is ~ 0.38 nm.

Having confirmed the validity of our approach, we next examine the substrate dependence. Since the lattice constants are different among the metals, we cannot use commensurate surface unit cells with the unit of polyethylene. Therefore, we calculated *n*-butane adsorption instead of polyethylene. The adsorption structure of *n*-alkane on the Pt(111) surface was studied intensively by Firment and Somorjai.²⁹ We adopted the same unit cell as that on Pt(111) for other hexagonal close-packed surfaces as shown in Fig. 1(c). For com-

TABLE II. Calculated adsorption energies E_{ad} , work-function change $\Delta\phi$, and $\nu(\text{CH})$ vibrational modes of polyethylene on Cu(100) as a function of molecule-surface distance Z_C . The calculated and experimental (Ref. 25) $\nu(\text{CH})$ vibrational frequencies of crystalline polyethylene are also shown.

Z_C (nm)	E_{ad} (kJ/mol/CH ₂)	$\Delta\phi$ (eV)	ν_1	ν_2	ν_3	ν_4
			(cm ⁻¹)			
0.431	-0.80	-0.11	2910	2914	2930	2978
0.405	-0.95	-0.21	2903	2909	2931	2975
0.392	-1.00	-0.28	2895	2902	2932	2972
0.378	-0.99	-0.36	2884	2896	2928	2967
0.351	-0.65	-0.58	2852	2870	2928	2962
0.325	+0.63	-0.87	2806	2843	2930	2957
Polyethylene crystal		Calculated	2913	2932	2935	2979
		Expt.		2848		2918

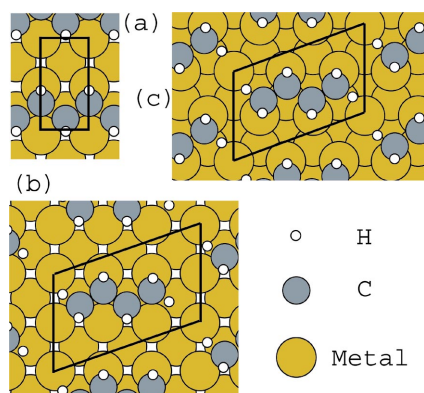


FIG. 1. (Color) Top views of (a) polyethylene adsorbed Cu(100) 1×2 surface, (b) *n*-butane adsorbed Cu(100) surface, and (c) *n*-butane adsorbed hexagonal close-packed surface. Surface unit cells are shown by solid lines.

parison, we also calculated *n*-butane adsorption on the Cu(100) surface as shown in Fig. 1(b). We optimized the structure of *n*-butane adsorbed on metal surfaces by fixing Z_C and the coordinates of the substrate metal atoms. To obtain $\Delta\phi$ of polyethylene adsorbed on the different surfaces, we assumed that the induced dipole moment of polyethylene on one metal surface is proportional to that of *n*-butane on the same metal surface. We confirmed this linearity on Cu(100), and obtained the linear coefficient of 0.432. To obtain $\Delta\nu(\text{CH}_p)$ of polyethylene on metal surfaces, we adopted the following prescriptions. We calculated force constants of stretching between C and H_p for polyethylene on Cu(100) [$f(\text{CH}_p)$] by varying Z_C , and made a map from the force constants to the $\nu(\text{CH})$ frequencies: $f(\text{CH}_p) \rightarrow \nu_1 \sim \nu_4$. We then calculated force constants of stretching between C and H_p for butane on other metal surfaces. By applying the map to the calculated force constants, we estimated the $\nu(\text{CH})$ frequencies of polyethylene on those metal surfaces. The calculated $\Delta\phi$ and $\Delta\nu(\text{CH}_p)$ of polyethylene adsorbed on metal surfaces are shown in Fig. 2 along with E_{ad} of *n*-butane on the same surfaces. We also compared calculated $\Delta\phi$ and $\Delta\nu(\text{CH}_p)$ with available experimental data and estimated the most probable Z_C as summarized in Table III. If

both $\Delta\nu(\text{CH}_p)$ and $\Delta\phi$ were reported, we adjusted Z_C to reproduce both of the experimental values as well as possible. If only one of them was reported, we adjusted Z_C to reproduce the experimental value.

As shown in Table III, our calculations give quite reasonable results for polyethylene not only on Cu(100) but also on Ag(111), where both $\nu(\text{CH})$ and $\Delta\phi$ were experimentally measured. One important information from Table III is that Z_C thus determined significantly depends on metal surfaces and the relative distance of the molecule to the surface largely determines $\Delta\phi$ and $\nu(\text{CH})$. As mentioned above, there is an experimentally observed trend that the magnitude of the interfacial dipole tends to increase as the substrate metal work function increases. Two of the present authors (H.I. and K.S.) suggested that the origin of the observed trend can be ascribed to the larger push back effect for metals of larger work functions because they have larger surface dipole layer formed by a larger penetration of electrons into vacuum.¹ However, from the present calculations, a different picture emerges. As shown in Fig. 2(a), if molecules are fixed at the same Z_C on various metals, the induced interfacial dipole moments do not follow the observed trend. For example, Ag(111) and Au(111) have very similar induced dipoles if *n*-alkane molecules are located at the same distance from the two surfaces. Therefore, we conclude that the distance between the adsorbate and the metal is an important factor determining the dependence of induced dipoles on metal substrates. Figure 2(b) also suggests important points regarding the softening of the $\nu(\text{CH})$ mode. Compared to surfaces of simple metals, i.e., Mg(001) and Al(111), noble-metal and transition-metal surfaces have more negative $\Delta\nu(\text{CH}_p)$, especially for $Z_C < 0.37$ nm. If the transition dipole-image dipole interaction is the dominant factor for the $\nu(\text{CH})$ softening,⁹ the $\nu(\text{CH})$ - Z_C curves on different metal surfaces should be identical except for the position of the image plane, being inconsistent with the present results. We also found that the projected density of states (PDOS) onto occupied butane molecular orbitals shows their original character upon adsorption on metal surfaces, while PDOS onto unoccupied molecular orbitals show hybridization with occupied substrate states. We ascribe the larger softening of the

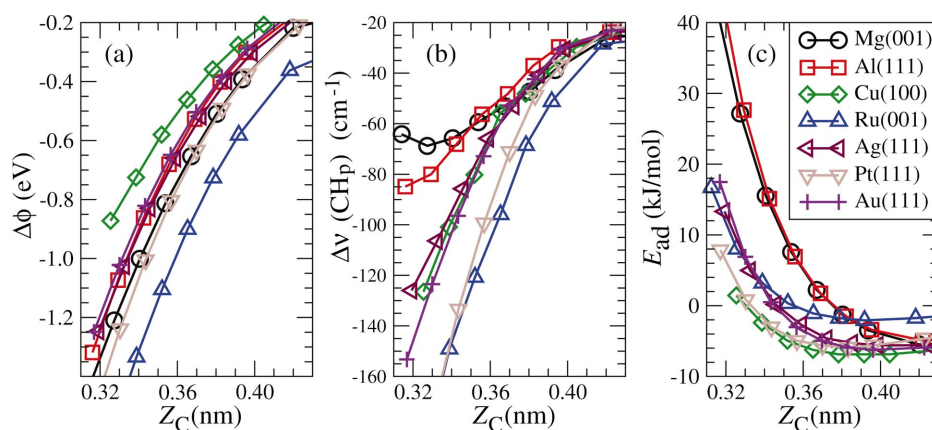


FIG. 2. (Color) The calculated (a) work-function change $\Delta\phi$, (b) CH stretching frequency shift $\Delta\nu(\text{CH}_p)$, and (c) the adsorption energies. Data in (a) and (b) are calculated for polyethylene adsorbed surfaces and those in (c) are for *n*-butane adsorbed surfaces.

TABLE III. Theoretically fitted C height Z_C , measured from the first layer surface atoms, the work-function change $\Delta\phi$, and the $\nu(\text{CH}_p)$ frequency shift $\Delta\nu(\text{CH}_p)$ for polyethylene on metal surfaces. Experimentally observed $\Delta\phi$ on Cu(100) (Ref. 23), Ag(111) (Ref. 30), and Au(111) (Ref. 30) and $\Delta\nu(\text{CH}_p)$ on Cu(100) (Ref. 24), Ru(001) (Ref. 31), Ag(111) (Ref. 9) and Pt(111) (Ref. 32) are also shown.

	Calculated results			Experimental results	
	Z_C (nm)	$\Delta\phi$ (eV)	$\Delta\nu(\text{CH}_p)$ (cm^{-1})	$\Delta\phi$ (eV)	$\Delta\nu(\text{CH}_p)$ (cm^{-1})
Cu(100)	0.383	-0.33	-44	-0.3	-48
Ru(001)	0.339	-1.34	-150		-150
Ag(111)	0.390	-0.36	-37	-0.5 ^a	-34
Pt(111)	0.356	-0.81	-100		-100
Au(111)	0.352	-0.70	-80	-0.7	

^aSubstrate is polycrystalline Ag.

$\nu(\text{CH}_p)$ mode on noble-metal and transition-metal surfaces to the hybridization between the molecular unoccupied states and the substrate d -band states, which is shown to be important for chemisorbed systems.³³ These facts give strong and direct evidences for the importance of the electronic interac-

tion between occupied substrate states with unoccupied molecular orbitals for the $\nu(\text{CH})$ mode softening.^{10,11}

In summary, we have studied the substrate dependence of work-function change and CH stretching mode softening for n -alkane adsorbed on various metal surfaces by using first-principles theoretical calculations. We showed that although DFT-GGA calculations cannot reproduce the physisorption energies well, the work-function change and CH stretching mode softening can be well reproduced. We found that the deduced molecule-surface distance at adsorption depends on metal substrate and this dominates the dependence of these adsorption-related properties on metal substrates.

We thank Professor J. K. Nørskov for valuable discussions and critical reading of the manuscript. This work was partly supported by Grant-in-Aid for Creative Scientific Research [Elucidation and control of interfaces related to organic electronic devices, Grant No. 14GS0213] and 21st Century COE Program (Establishment of COE of Materials Science: Elucidation and Creation of Molecular Functions) from the Ministry of Education, Culture, Science, Sports, and Technology (MEXT), Japan, and Tsukuba Advanced Computing Center (TACC) project. Numerical calculations were carried out at computer centers of Kyoto University, Nagoya University, and TACC.

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